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journal homepage: [www.elsevier.com/locate/mssp](http://www.elsevier.com/locate/mssp)

## Plasmonic enhanced photocatalytic activity of semiconductors for the degradation of organic pollutants under visible light

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## ARTICLE INFO

## Article history:

Received 5 May 2015

Received in revised form

2 August 2015

Accepted 28 August 2015

## Keywords:

Plasmonic nanoparticles

Semiconductors

Laser assisted catalysis

Photocatalyst

Bisphenol-A

Photodegradation

Water treatment

## ABSTRACT

Metal oxide semiconductors hold great promise for applications in energy conversion and storage, environmental remediation, and other areas. However, critical factors such as the high rate of charge-carrier recombination and limited light absorption have restricted more practical and viable applications. In this context, plasmonic nanostructures of noble metals in combination with semiconductors offer a promising future for the next generation of energy needs. In this work we investigate the coupling between Plasmonic gold nanostructures and catalyst supports such as TiO<sub>2</sub>, ZnO and Al<sub>2</sub>O<sub>3</sub> in order to study the photocatalytic degradation of Bisphenol A (BPA) under visible irradiation (laser source and LED). The experimental investigations have shown extremely fast and complete photodegradation of organic pollutants in water. The influence of laser power and photocatalyst band gap on the catalytic activity was investigated as well. Au/TiO<sub>2</sub> catalyst showed the fastest degradation of BPA due to efficient electron transfer from excited noble metal gold nanoparticles to the semiconductor.

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### 1. Introduction

Natural water environments today are treated by a variety of chemical substances derived from man-made products such as colorants and organochlorine and aromatic hydrocarbons. In particular, Bisphenol A (BPA), which is used as a monomer and additive in the production of polycarbonate plastics, causes a strong estrogenic endocrine disrupting effect [1] and cancer [2]. It has an acute toxicity in the range of ~1–10 mg L<sup>-1</sup> for a number of fresh water and marine species [3]. Thus development of methods for the removal of BPA is a big challenge. In this context, advanced oxidation processes (AOPs) have been proposed for the elimination of many toxic organic compounds in waste water, air and soil; such as (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>, UV/H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>, and UV/TiO<sub>2</sub>). More particularly, the photocatalytic process using a semiconductor as photocatalyst (PC) under UV irradiation is currently applied for the oxidation of various organic compounds [4,5]. The semiconductors adsorb photons to create active electrons and holes; among many

difficulties, two major ones are the low photocatalytic efficiency and the lack of satisfactory visible-light-responsive photocatalytic materials [6]. The former is mainly due to the fast recombination of excited electrons and holes [7]. The other difficulty is that many high performance photocatalytic materials like ZnO and TiO<sub>2</sub> have large band gaps and only absorb the light in the near ultraviolet region (< 380 nm). The use of UV light requires artificial light sources making it less attractive when energy supply and cost become a big concern [7]. The need to use sunlight more efficiently has sparked increasing research interest in visible light photocatalysis. Various solutions have been reported and shown that the possibility to increase the efficiency of semiconductor photocatalysis such as coupling them with noble metals or doping them with nitrogen [5]. Plasmonic nanostructures of noble metals have been attracting significant attention for their ability to interact with light from visible to near IR range through the creation of localized surface plasmon resonance (LSPR). Moreover, the LSPR is responsible for the electromagnetic-field enhancement [8] that leads to surface-enhanced Raman scattering (SERS) and other surface-enhanced spectroscopic processes. The excitation of LSPR has been investigated in a wide range of biosensing applications [9,10] and for the detection of small amount of organic molecules [11,12]. Coupling plasmonic NPs with photocatalyst materials has

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recently facilitated the rapid progress in enhancing photocatalytic efficiency under visible light irradiation, increasing the prospect of using sun light for environmental and energy applications such as waste water treatment [13,14]. Plasmonic photocatalysis makes use of noble metal nanoparticles in contact with semiconductor and possesses two features: a Schottky junction and localized surface plasmonic resonance (LSPR). In that context, gold nanoparticles (GNPs) in electronic contact with  $\text{TiO}_2$  have shown the possibility to use this later as efficient PC in the visible range [7,15].

In this work, we combine plasmonic effect of GNPs with  $\text{TiO}_2$  and ZnO in order to make it possible the photodegradation of BPA under visible laser and LED irradiation. The influence of various parameters such as irradiation time, laser power, and catalyst type was investigated. Four materials ( $\text{Au/TiO}_2$ ,  $\text{Au/Al}_2\text{O}_3$ ,  $\text{Au/ZnO}$  and  $\text{TiO}_2$ ) were investigated as PCs for the degradation of BPA under 2230 mW of 532-nm laser. Also photocatalytic degradation of BPA under green light emitting diode (LED) was demonstrated.

## 2. Experimental

$\text{Au/TiO}_2$ ,  $\text{Au/Al}_2\text{O}_3$ ,  $\text{Au/ZnO}$  catalysts were purchased from STREM chemicals. They consist of 1% gold on anatase titaniumdioxide extrudates ( $\text{BET}=40\text{--}50\text{ m}^2/\text{g}$ ), zinc oxide granulate ( $\text{BET}=40\text{--}50\text{ m}^2/\text{g}$ ) and aluminum oxide extrudates ( $\text{BET}=200\text{--}260\text{ m}^2/\text{g}$ ) where they have a dark purple color with GNPs having size 2–3 nm. The plasmon resonance band is around 532 nm (Fig. 1).

$\text{TiO}_2$  extrudates (manufacturer: Saint Gobain NORPRO) exhibiting a 100% anatase structure from our XRD analysis and measured specific surface area of  $107\text{ m}^2/\text{g}$  was used to study the influence of GNPs. The photocatalytic activity was investigated using 2.5 ml of BPA (0.1 mM) and 10 mg of catalyst in a quartz cuvette under visible irradiation. A laser emitting at 532 nm was used as a visible source to irradiate the solution through the quartz cuvette. The laser power can be adjusted from 10 to 2230 mW. Using this laser, the influence of incident energy on the catalytic activity can be studied. The same catalytic experiment was performed using green light diode (LED) (power=100 mw). During the irradiation, the solution of BPA was magnetically stirred. The absorbance of BPA was measured by UV-visible spectrometry before and after irradiation for studying the reaction kinetics.

## 3. Results and discussion

The results shown in Fig. 2A indicate that no conversion of BPA in the presence of  $\text{TiO}_2$  under laser light irradiation. Additionally, the conversion rate is almost negligible with  $\text{Au/Al}_2\text{O}_3$  (less than 5% after 30 min). In the opposite, 92% of BPA is eliminated after 12 min in the presence of  $\text{Au/TiO}_2$ .  $\text{Au/ZnO}$  shows also catalytic activity (~50% of conversion after 30 min) but seems to be less efficient than  $\text{Au/TiO}_2$  (100% of conversion after 20 min). It appears from this first result that the photodegradation reaction is directly related to the presence of GNPs at the surface of both  $\text{TiO}_2$  and ZnO which are semiconductors with band gaps of 3.2 and 3.37 eV respectively. The catalytic activity under visible light could be attributed to electrons generated during excitation of the localized surface plasmon resonance (LSPR) which could be transferred to the conduction band (CB) of the semiconductor. Indeed, during laser excitation of GNPs, electrons are very dynamic in a high energy level that is higher than the CB of  $\text{TiO}_2$  and this of ZnO. The electrons transferred in this way are used for the generation of  $\text{OH}^\bullet$  radicals from water and dissolved oxygen at the surface of  $\text{TiO}_2$ .  $\text{OH}^\bullet$  are highly reactive species and responsible for the

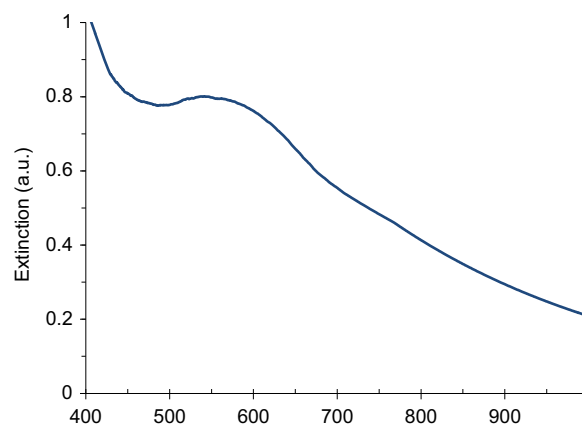


Fig. 1. Extinction spectrum of the  $\text{Au/TiO}_2$  photocatalyst showing a maximum of resonance around 532 nm.

degradation of pollutants.

The absence of catalytic activity of  $\text{Au/Al}_2\text{O}_3$  under 532 nm is simply related to the absence of electron transfer from GNPs to  $\text{Al}_2\text{O}_3$ . Indeed, even though GNPs absorb visible photons, the high energy gap of  $\text{Al}_2\text{O}_3$  (> 6.5 eV) makes it difficult the electron transfer.

The kinetics of photocatalytic degradation of BPA in the presence of  $\text{Au/TiO}_2$ ,  $\text{Au/ZnO}$  and  $\text{Au/Al}_2\text{O}_3$  has shown to follow first order kinetics where  $\ln C_0/C$  varies linearly with time (Fig. 1B). The constant rate of reaction ( $K$  in  $\text{min}^{-1}$ ) for  $\text{Au/Al}_2\text{O}_3$ ,  $\text{Au/ZnO}$  and  $\text{Au/TiO}_2$  is 0.0017, 0.0258 and 0.225 respectively (Fig. 2B). Indeed, this result shows clearly faster degradation reaction in the presence of  $\text{Au/TiO}_2$ . This behavior is due to efficient electron transfer promoted by the highest difference of energy gap between excited electrons of GNPs and CB of  $\text{TiO}_2$ .

Fig. 3 shows the influence of laser power (LP) on the catalytic activity of  $\text{Au/TiO}_2$ . From Fig. 3A, it appears that the conversion rate at a given time is increasing with incident energy, in relation with higher number of transferred electrons. However, the variation of  $K$  with LP (Fig. 3B) seems to reach a plateau after 1000 mW where conversion rate of BPA after 9 min is almost the same, even for 2230 mW. This saturation of  $K$  could be attributed to a limited number of transferred electrons in relation with small amount of gold which is 1 wt% from  $\text{TiO}_2$  weight.

The same experiment was performed in the presence of green LED. The experimental results of the photocatalytic degradation of BPA in the presence of  $\text{Au/TiO}_2$  are shown in Fig. 4A, where the conversion rate is 78% after 1 h. As shown in Fig. 4B, the photocatalytic degradation of BPA obeys the first order reaction kinetics with a constant of reaction of  $0.0224\text{ min}^{-1}$ .

Thermal effect is known to be an important issue when studying the reaction kinetics. In our experiments, no heating of the solution was observed in the presence of  $\text{TiO}_2$ . However, a temperature increase of the solution was observed for  $\text{Au/TiO}_2$ ,  $\text{Au/ZnO}$  and  $\text{Au/Al}_2\text{O}_3$  where GNPs absorb incident energy and convert it into heat. Indeed, small gold nanospheres have plasmonic resonance band in the green range and can absorb a significant part of the incident laser intensity. The excitation of this band at 532 nm leads to an enhancement of the electromagnetic field at the particle surface [8]. Some of this concentrated energy is converted into heat [16]. The temperature can reach  $50^\circ\text{C}$  after few minutes of laser irradiation at 2230 mW. The final temperature is the same whatever the catalyst material as they contain the same amount of GNPs. The temperature of the solution increases as the intensity of laser increases, to reach 23, 35, 43 and  $50^\circ\text{C}$  at 100, 500, 1000 and 2230 mW respectively. Indeed, this temperature increase could affect the kinetics of degradation reaction.

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